Incremental model identification of reaction systems

Diogo Rodrigues, Sriniketh Srinivasan, Nirav Bhatt, Julien Billeter, Michael Amrhein, Dominique Bonvin

Laboratoire d’Automatique
Ecole Polytechnique Fédérale de Lausanne

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Outline

- Models of reaction systems and concept of extents
  - Homogeneous reaction systems
  - Distributed reaction systems
  - Generalization to other reaction systems
  - Applications of extents

- Model identification
  - Simultaneous model identification
  - Incremental model identification
  - Example

- Conclusions
Homogeneous reaction systems

Balance equations

Nonisothermal homogeneous reaction system consisting of $S$ species, $R$ independent reactions, $p$ inlet streams, and 1 outlet stream

Mole balances for $S$ species

$$\dot{n}(t) = N^T r_v(t) + W_{in} u_{in}(t) - \omega(t) n(t), \quad n(0) = n_0$$

$$\begin{align*}
(S) & \quad (S \times R) (R) & \quad (S \times p) (p) \quad r_v(t) := V(t) r(t), \quad \omega(t) := \frac{u_{out}(t)}{m(t)}
\end{align*}$$

Mass $m$, volume $V$ and molar concentrations $c$

$$\begin{align*}
m(t) &= 1^T_S M_w n(t), & V(t) &= \frac{m(t)}{\rho(t)}, & c(t) &= \frac{n(t)}{V(t)}
\dot{m}(t) &= 1^T_p u_{in}(t) - u_{out}(t), & m(0) &= m_0
\end{align*}$$

Global macroscopic view

Valid regardless of temperature, catalyst or solvent

Redundant information $m(t)$
Homogeneous reaction systems

**Objective:** Decoupled reaction system in terms of vessel extents

- **S-dimensional model equations**

\[
\dot{n}(t) = \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t)n(t), \quad n(0) = n_0
\]

- **Decoupled reaction model in terms of vessel extents**

\[
\begin{align*}
\dot{x}_{r,i}(t) &= r_{v,i}(t) - \omega(t)x_{r,i}(t) \quad x_{r,i}(0) = 0 \quad i = 1, \ldots, R \\
\dot{x}_{in,j}(t) &= u_{in,j}(t) - \omega(t)x_{in,j}(t) \quad x_{in,j}(0) = 0 \quad j = 1, \ldots, p \\
\dot{x}_{ic}(t) &= -\omega(t)x_{ic}(t) \quad x_{ic}(0) = 1
\end{align*}
\]

- **Vessel extents** are extents discounted by the amount of material that has left the reactor

- System of dimension \( d := (R + p + 1) \)

- Only **apparent decoupling** as \( r_{v,i}(t) \) is an endogenous input and not an independent input!
Homogeneous reaction systems

Procedure: Four-way decomposition into extents and invariants

- Model with zero initial conditions

\[ \dot{n}(t) = N^T r_v(t) + W_{in} u_{in}(t) + n_0 \delta(t) - \omega(t) n(t), \quad n(0) = 0_S \]

- Assumption: \( \text{rank } [N^T \ W_{in} \ n_0] = R + p + 1 \). Linear transformation

\[
\begin{bmatrix}
  x_r(t) \\
  x_{in}(t) \\
  x_{ic}(t) \\
  x_{iv}(t)
\end{bmatrix} = T \begin{bmatrix}
  n(t)
\end{bmatrix} \quad T = [N^T \ W_{in} \ n_0 \ P]^{-1} \quad [N^T \ W_{in} \ n_0]^T P = 0_{d \times q}
\]

- Vessel extents of reaction \( x_r \), inlet \( x_{in} \), initial conditions \( x_{ic} \), and invariants \( x_{iv} \)

\[
\begin{align*}
  \dot{x}_r(t) &= r_v(t) - \omega(t) x_r(t) \quad x_r(0) = 0_R \\
  \dot{x}_{in}(t) &= u_{in}(t) - \omega(t) x_{in}(t) \quad x_{in}(0) = 0_p \\
  \dot{x}_{ic}(t) &= -\omega(t) x_{ic}(t) \quad x_{ic}(0) = 1 \\
  x_{iv}(t) &= 0_q
\end{align*}
\]

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Homogeneous reaction systems

Four subspaces, transformation possible if $S \geq R + p + 1$

\[ \mathcal{T} = \begin{bmatrix} R \\ F \\ i^T \\ P^+ \end{bmatrix} = \begin{bmatrix} N^T & W_{in} & n_0 & P \end{bmatrix}^{-1} \]

\[ \begin{bmatrix} x_r(t) \\ x_{in}(t) \\ x_{ic}(t) \\ x_{iv}(t) \end{bmatrix} = \mathcal{T} \mathbf{n}(t) \]

\[ \mathbf{n}(t) = N^T x_r(t) + W_{in} x_{in}(t) + n_0 x_{ic}(t) \]

\[ x_{iv}(t) = P^+ \mathbf{n}(t) = 0_q \]

S-dimensional space of species

\[ d = R + p + 1 \text{ variants} \]
\[ q = S - R - p - 1 \text{ invariants} \]
Homogeneous reaction systems

**Example:** Ethanolysis reaction in an homogeneous CSTR

- Seven species \((S = 7)\), three reactions \((R = 3)\), two inlets \((p = 2)\) and one outlet
- Stoichiometric matrix \(N\), inlet-composition matrix \(W_{in}\) and initial conditions \(n_0\):

\[
N = \begin{bmatrix}
-1 & -1 & 1 & 1 & 0 & 0 & 0 \\
0 & -1 & 1 & 1 & 0 & 0 & 0 \\
0 & -1 & 0 & -1 & 0 & 1 & 1
\end{bmatrix}
\]

\[
W_{in} = \begin{bmatrix}
w_{in,A} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & w_{in,B} & 0 & 0 & 0 & 0 & 0
\end{bmatrix}^T
\]

\(n_0\)

![Diagram of reaction system](image)

**Numbers of moles**

![Graph of numbers of moles over time](image)

**Reaction extents?**
Homogeneous reaction systems

Example: Computation of extents

- Fewer extents than numbers of moles
- Extents are more prone to have mathematically well-defined shapes such as monotonicity, convexity/concavity

\[
\mathcal{T} = \begin{bmatrix} R & F \end{bmatrix}^T
\]

One invariant \( x_{iv}(t) = P^+ n(t) = 0 \)
Mole balances for $S$ species:

$$\frac{\partial c(z, t)}{\partial t} + \nu \frac{\partial c(z, t)}{\partial z} = N^T r(z, t), \quad c(0, t) = c_{in}(t), \quad c(z, 0) = c_0(z)$$

To an observer sitting on a particle of velocity $\nu$, $c(z, t)$ and $r(z, t)$ are viewed as $c_p(\tau)$ and $r_p(\tau)$, with $z = \nu \tau$ and $t = \tau$, where $\tau$ is the time spent in the reactor up to position $z$.

It follows that $\frac{dc_p}{d\tau} = \frac{\partial c}{\partial z} \left( \frac{dz}{d\tau} \right) + \frac{\partial c}{\partial t} \left( \frac{dt}{d\tau} \right) = \frac{\partial c}{\partial z} \nu + \frac{\partial c}{\partial t}$, and the system of PDEs becomes a system of ODEs:

$$\frac{d}{d\tau} c_p(\tau) = N^T r_p(\tau), \quad c_p(0) = c_{in}(0)$$

Deviation variables $\delta c_p := c_p - c_{in}(0)$ without effect of boundary conditions:

$$\frac{d}{d\tau} \delta c_p(\tau) = N^T r_p(\tau), \quad c_p(0) = 0_S$$

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Let \( \text{rank}(N^T) = R \) and consider the matrix \( T = [N^T \ P]^{-1} \), where \( NP = 0_{R \times q} \). Then, \( T \) partitions \( \delta c_p \) into two contributions:

\[
\begin{bmatrix}
    x_{p,r}(\tau) \\
    x_{p,iv}(\tau)
\end{bmatrix} = T \delta c_p(\tau) =
\begin{bmatrix}
    T_r \ \\
    T_{iv}
\end{bmatrix} \delta c_p(\tau)
\]

Dynamic equations:

\[
\frac{d}{d\tau} x_{p,r}(\tau) = r_p(\tau), \quad x_{p,r}(0) = 0_R
\]

\[
x_{p,iv}(\tau) = 0_q
\]

Reconstruction:

\[
c_p(\tau) = N^T x_{p,r}(\tau) + c_{in}(0)
\]

Generalization to other reaction systems

- Homogeneous reaction systems with heat balance\(^4\)
  - Additional heat balance equation
  - Additional decoupled extent of heat exchange

- Gas-liquid reaction systems\(^5\)
  - Balance equations for both the gas and liquid phases
  - Additional decoupled extents of mass transfer

- Reaction systems with instantaneous equilibria\(^6\)
  - Balance equations for components conserved by equilibria
  - Extents of kinetically controlled reactions

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Applications of extents

- **Linear state transformation**
  - From concentrations and temperatures to decoupled extents
  - Systematic generation of invariant relationships

- **Minimal dimensionality**
  - Redundant states can be eliminated → model-order reduction
  - Invariant relationships → algebraic constraints for data reconciliation

- **Decoupled states**
  - Each state is related to a single rate process
  - Rates can be identified individually → incremental approach with fewer parameters → global optimization
  - Possibility of having additional ($0^{th}$, $1^{st}$ and $2^{nd}$-order) constraints on the extents → improved data reconciliation, state estimation, ALS, etc.
Applications of extents

- Useful for the investigation of reaction systems:
  - **Kinetic model identification**
  - State reconstruction via invariant relationships\(^7\)
  - Data reconciliation via invariant relationships and shape constraints\(^7\)
  - State estimation via invariant relationships and shape constraints\(^8\)
  - Control via rate estimation\(^9\)
  - Static RTO via rate estimation\(^10\)
  - Model reduction via singular perturbation\(^10\)

- Generally applicable
  - To most reaction systems and reactor types
  - In principle, to systems with more balance equations than rates

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  - Incremental model identification
  - Example

- Conclusions
Model identification

- Given experimental concentrations
- Identify unknown functions for the reaction rates
- Subject to a set of candidate models for all reactions
Model identification
Simultaneous and incremental approaches

Experimental values

Model predictions

Experimental data flow
Simulated data flow
Information flow
Identified rate laws

Thick: data regarding the global reaction system
Thin: data specific to a single reaction or mass transfer

Laboratory measurements

Laboratory measurements

Simultaneous approach
Extent-based incremental approach

Experimental data flow
Simulated data flow
Information flow
Identified rate laws

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Simultaneous model identification

- Define a model candidate for all rate processes.
- Estimate parameters in the model by solving the following problem:

\[
\min_{\theta} \sum_{h=1}^{H} \left( \hat{n}(t_h) - \tilde{n}(t_h, \theta) \right)^T W(t_h) \left( \tilde{n}(t_h) - \hat{n}(t_h, \theta) \right)
\]

s.t.
\[
\dot{\hat{n}}(t, \theta) = N^T V(t) r(\hat{c}(t, \theta), \theta) + W_{in} u_{in}(t) - \omega(t) \hat{n}(t, \theta), \quad \hat{n}(0, \theta) = n_0
\]
\[
\hat{c}(t, \theta) = \frac{\hat{n}(t, \theta) - \omega(t) \hat{n}(t, \theta)}{V(t)}
\]

- Repeat the procedure for all combinations of model candidates.
- The set of model candidates with the best fit is chosen.
Simultaneous model identification leads to optimal parameter estimates in a maximum-likelihood sense for correct model structure.

But it is computationally costly:
- The procedure must be repeated for all combinations of rate candidates
- Convergence is difficult due to the large number of parameters

Rate-based incremental model identification was initially proposed to identify the correct model structure efficiently\(^{12}\)

Extent-based incremental model identification provides tighter confidence intervals and improved model discrimination\(^{13}\)

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For the $i$th reaction, estimation of kinetic parameters $\theta_i$ by comparing the experimental extent $\tilde{x}_{r,i}$ with the modeled extent $\hat{x}_{r,i}$, which approximates

$$\dot{x}_{r,i}(t) = V(t) r_i(c(t), \theta_i) - \omega(t) x_{r,i}(t) \quad x_{r,i}(0) = 0.$$ 

Experimental extent $\tilde{x}_{r,i}(t_h)$ is given by a linear transformation of $V(t_h)\tilde{c}(t_h)$

- Requires measurements $\tilde{c}(t_h)$, $V(t_h)$, $\omega(t_h)$
Incremental model identification (IMI_n)

- Compute $x_r(t)$ for all $R$ reactions

- Identify the model for each reaction individually\(^{14}\)

\[
\begin{align*}
\min_{\theta_i^{(m_i)}} \quad & J(\theta_i^{(m_i)}) = \sum_{h=1}^{H} \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) W_i(t_h) \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) \\
\text{s.t.} \quad & \hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}) = V(t) \hat{r}_i^{(m_i)}(\tilde{c}(t), \theta_i^{(m_i)}) - \omega(t) \hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}), \quad \hat{x}_{r,i}^{(m_i)}(0, \theta_i^{(m_i)}) = 0.
\end{align*}
\]

- Model $m_i$ with the least objective function is the best model

- Use simultaneous approach as final step for optimal parameter estimates

---

If a reaction rate law \( r \) is linear in \( L \) parameters \( \alpha \) and nonlinear in \( \theta \):

\[
r(c(t), \alpha, \theta) = r_0(c(t), \theta) + \sum_{\ell=1}^{L} \alpha_\ell r_\ell(c(t), \theta)
\]

Assuming the \( i \)th reaction rate is \( r \), the integral solution of \( x_{r,i} \) is:

\[
x_{r,i}(t) = V(t)d_0(t) + \sum_{\ell=1}^{L} \alpha_\ell V(t)d_\ell(t),
\]

where \( d_\ell(t) := \int_0^t \frac{V(\tau)}{V(t)} r_\ell(c(\tau), \theta) e^{-\int_{\tau}^t \omega(\zeta) d\zeta} d\tau \) is estimated as \( \hat{d}_\ell(t_h, \theta) \) from \( \hat{r}_\ell(\tilde{c}(t_h), \theta), V(t_h), \omega(t_h) \)

Modeled extent \( \hat{x}_{r,i}(t_h, \alpha, \theta) := V(t_h)\hat{d}_0(t_h, \theta) + \sum_{\ell=1}^{L} \alpha_\ell V(t_h)\hat{d}_\ell(t_h, \theta) \) is linear in \( \alpha \)
The identification problem is

\[
\min_{\alpha, \theta} J(\alpha, \theta) = \sum_{h=1}^{H} \frac{1}{H} \left( \frac{\hat{x}_{r,i}(t_h, \alpha, \theta) - \check{x}_{r,i}(t_h)}{V(t_h)} \right)^2
\]

The cost function is quadratic in \(\alpha\):

\[
J(\alpha, \theta) = c(\theta) + 2\alpha^T g(\theta) + \alpha^T H(\theta) \alpha
\]

The optimal parameters \(\alpha\) for each \(\theta\) are \(\hat{\alpha}(\theta) = -H(\theta)^{-1} g(\theta)\), and the optimization problem is reformulated with only the decision variables \(\theta\):

\[
\min_{\theta} \bar{J}(\theta) = J(\hat{\alpha}(\theta), \theta) = c(\theta) - g(\theta)^T H(\theta)^{-1} g(\theta)
\]

Problem with few decision variables, solved efficiently to global optimality\(^{15}\)

Incremental model identification (IMIş)

- Identify the model for each reaction individually, by postulating rate expressions with extents as arguments\(^\text{16}\)

\[
\min_{\theta_i^{(m_i)}} J(\theta_i^{(m_i)}) = \sum_{h=1}^{H} \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) W_i(t_h) \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) \\
\text{s.t. } \dot{\hat{x}}^{(m_i)}_{r,i}(t, \theta_i^{(m_i)}) = V(t) \phi_{x,i}^{(m_i)}(\hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}), \tilde{x}_{r,J}(t), \theta_i^{(m_i)}) - \omega(t) \hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}), \\
\hat{x}_{r,i}^{(m_i)}(0, \theta_i^{(m_i)}) = 0.
\]

- \(\tilde{x}_{r,J}\) are the \((R - 1)\) measured extents that need to be interpolated

- Model \(m_i\) with the least objective function is the best model

- Use simultaneous approach as final step for optimal parameter estimates

---

Incremental model identification
Plug-flow reactors\textsuperscript{17}

- Identification of the rate expression $r_i$ and estimation of the parameters $\theta_i$:

$$\min_{\theta_i} \sum_{p=1}^{P} \sum_{h=1}^{H} \left( \hat{x}_{r,i}(z_p, t_h) - \hat{x}_{r,i}(z_p, t_h, \theta_i) \right)^2$$

s.t. $\frac{\partial}{\partial t} \left( \hat{x}_{r,i}(z, t, \theta_i) \right) + v \frac{\partial}{\partial z} \left( \hat{x}_{r,i}(z, t, \theta_i) \right) = \hat{r}_i(\bar{c}(z, t), \theta_i)$, $\hat{x}_{r,i}(z, 0, \theta_i) = \hat{x}_{r,i}(0, t, \theta_i) = 0$

- Accurate for frequent measurements along the reactor: difficult in practice
- But $\bar{c}_p(\tau_h)$ are concentrations at the reactor exit $z_e$ with the velocity $v_h = \frac{z_e}{\tau_h}$
- Identification problem reformulated as:

$$\min_{\theta_i} \sum_{h=1}^{H} \left( \hat{x}_{p,r,i}(\tau_h) - \hat{x}_{p,r,i}(\tau_h, \theta_i) \right)^2$$

s.t. $\frac{d}{d\tau} \hat{x}_{p,r,i}(\tau, \theta_i) = \hat{r}_{p,i}(\bar{c}_p(\tau), \theta_i)$, $\hat{x}_{p,r,i}(0, \theta_i) = 0$

Consider the acetoacetylation of pyrrole in a semi-batch reactor

The reaction system consists of seven species \( (S = 7) \) involved in four independent reactions \( (R = 4) \)

\[
\begin{align*}
R1 : & \quad A + B \rightarrow C \\
R2 : & \quad B + B \rightarrow D \\
R3 : & \quad B \rightarrow E \\
R4 : & \quad B + C \rightarrow F
\end{align*}
\]

Reactions R1, R2 and R4 are catalyzed by species K

The reactor initially contains 4 mol of A, 0.5 mol of B, 0.1 mol of C and 1 mol of catalyst K

Pure diketene (B) is fed into the reactor at the constant volumetric flowrate 0.1 L min\(^{-1}\)
Example: Acetoacetylation of pyrrole

Material balance equations:

\[
\begin{align*}
\dot{n}_A(t) &= -V(t) r_1(t) \\
\dot{n}_B(t) &= -V(t) r_1(t) - 2V(t) r_2(t) - V(t) r_3(t) - V(t) r_4(t) + w_{in,B} u_{in}(t) \\
\dot{n}_C(t) &= V(t) r_1(t) - V(t) r_4(t) \\
\dot{n}_D(t) &= V(t) r_2(t) \\
\dot{n}_E(t) &= V(t) r_3(t) \\
\dot{n}_F(t) &= V(t) r_4(t) \\
\dot{n}_K(t) &= 0
\end{align*}
\]

- The simulated numbers of moles of each species are corrupted by additive zero-mean Gaussian noise of standard deviation corresponding to \( \alpha \)% of its maximum value.

- Data sets are generated for 1000 different noise realizations.
Example: Acetoacetylation of pyrrole

A list of rate candidates is available for each reaction

<table>
<thead>
<tr>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1}^{(1)} = k_1 c_A c_B c_K$</td>
<td>$r_{2}^{(1)} = k_2 c_B^2 c_K$</td>
<td>$r_{3}^{(1)} = k_3 c_B$</td>
<td>$r_{4}^{(1)} = k_4 c_B c_C c_K$</td>
</tr>
<tr>
<td>$r_{1}^{(2)} = k_1 c_B$</td>
<td>$r_{2}^{(2)} = k_2 c_B$</td>
<td>$r_{3}^{(2)} = k_3 c_B^2$</td>
<td>$r_{4}^{(2)} = k_4 c_C$</td>
</tr>
<tr>
<td>$r_{1}^{(3)} = k_1 c_A$</td>
<td>$r_{2}^{(3)} = k_2 c_B^2$</td>
<td>$r_{3}^{(3)} = k_3 c_B c_K$</td>
<td>$r_{4}^{(3)} = k_4 c_B$</td>
</tr>
<tr>
<td>$r_{1}^{(4)} = k_1 c_K$</td>
<td>$r_{2}^{(4)} = k_2 c_B c_K$</td>
<td>$r_{3}^{(4)} = k_3 c_B^2 c_K$</td>
<td>$r_{4}^{(4)} = k_4 c_B c_C$</td>
</tr>
<tr>
<td>$r_{1}^{(5)} = k_1 c_A c_B$</td>
<td>$r_{2}^{(5)} = k_2 c_K$</td>
<td>$r_{3}^{(5)} = k_3 c_K$</td>
<td>$r_{4}^{(5)} = k_4 c_C c_K$</td>
</tr>
<tr>
<td>$r_{1}^{(6)} = k_1 c_A c_K$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{1}^{(7)} = k_1 c_B c_K$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{1}^{(8)} = k_1 c_A^2 c_K$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example: Acetoacetylation of pyrrole

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_{true}$</th>
<th>Data set</th>
<th>$\alpha$</th>
<th>$#/1000$</th>
<th>$k^*$</th>
<th>$\sigma_{k^*}$</th>
<th>$#/1000$</th>
<th>$k^*$</th>
<th>$\sigma_{k^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.0530</td>
<td>D1</td>
<td>1%</td>
<td>995</td>
<td>0.0529</td>
<td>0.0009</td>
<td>1000</td>
<td>0.0530</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>5%</td>
<td>733</td>
<td>0.0523</td>
<td>0.0041</td>
<td>942</td>
<td>0.0529</td>
<td>0.0023</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D3</td>
<td>10%</td>
<td>483</td>
<td>0.0519</td>
<td>0.0075</td>
<td>731</td>
<td>0.0530</td>
<td>0.0045</td>
</tr>
<tr>
<td>R2</td>
<td>0.1280</td>
<td>D1</td>
<td>1%</td>
<td>992</td>
<td>0.1275</td>
<td>0.0013</td>
<td>1000</td>
<td>0.1279</td>
<td>0.0007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>5%</td>
<td>764</td>
<td>0.1250</td>
<td>0.0059</td>
<td>940</td>
<td>0.1271</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D3</td>
<td>10%</td>
<td>425</td>
<td>0.1218</td>
<td>0.0114</td>
<td>924</td>
<td>0.1265</td>
<td>0.0059</td>
</tr>
<tr>
<td>R3</td>
<td>0.0280</td>
<td>D1</td>
<td>1%</td>
<td>983</td>
<td>0.0280</td>
<td>0.0001</td>
<td>984</td>
<td>0.0280</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>5%</td>
<td>870</td>
<td>0.0279</td>
<td>0.0006</td>
<td>818</td>
<td>0.0279</td>
<td>0.0006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D3</td>
<td>10%</td>
<td>833</td>
<td>0.0278</td>
<td>0.0011</td>
<td>756</td>
<td>0.0278</td>
<td>0.0010</td>
</tr>
<tr>
<td>R4</td>
<td>0.0030</td>
<td>D1</td>
<td>1%</td>
<td>749</td>
<td>0.0035</td>
<td>0.0032</td>
<td>999</td>
<td>0.0028</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>5%</td>
<td>335</td>
<td>0.0038</td>
<td>0.0056</td>
<td>994</td>
<td>0.0028</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D3</td>
<td>10%</td>
<td>236</td>
<td>0.0035</td>
<td>0.0059</td>
<td>866</td>
<td>0.0028</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

- $\text{IMI}_x$ performs better than $\text{IMI}_n$ in identifying the model structures
Outline

- Models of reaction systems and concept of extents
  - Homogeneous reaction systems
  - Distributed reaction systems
  - Generalization to other reaction systems
  - Applications of extents

- Model identification
  - Simultaneous model identification
  - Incremental model identification
  - Example

- Conclusions
Conclusions

- Divide-and-conquer strategy – decoupling provided by extents enables model identification of one reaction at a time.

- Incremental approach allows correct model discrimination and estimates accurately the parameter values.

- This approach avoids the drawbacks of the simultaneous approach.

- Can the incremental approach yield optimal parameter estimates and maintain its advantages? How and in which case?
Thank you for your attention!